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Parametric study of the explosivity of graphite-metals mixtures

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ABSTRACT

The explosivity of dust clouds is greatly influenced by several parameters which depend on the operating conditions, such as the initial turbulence, temperature or ignition energy, but obviously also on the materials composition. In the peculiar case of a mixture of two combustible powders, the physical and chemical properties of both dusts have an impact on the cloud flammability and on its explosivity. Nevertheless, no satisfactory 'mixing laws' predicting the mixture behavior are currently available and the composition variable to be considered for such models greatly depend on the safety parameters which have to be determined: from volume ratios for some thermal exchanges and ignition phenomena, to surface proportions for some heterogeneous reactions and molar contents for chemical reactions. This study is mainly focused on graphite/magnesium mixtures as they are encountered during the decommissioning activities of UNGG reactors (Natural Uranium Graphite Gas). Due to the different nature and reactivity of both powders, these mixtures offer a wide range of interests. Firstly, the rate-limiting steps for the combustion of graphite are distinct from those of metals (oxygen diffusion or metal vaporization). Secondly, the flame can be thickened by the presence of radiation during metal combustion, whereas this phenomenon is negligible for pure graphite. Finally, the turbulence of the initial dust cloud is modified by the addition of a second powder. In order to assess the explosivity of graphite/magnesium clouds, a parametric study of the effects of storage humidity, particle size distribution, ignition energy, and initial turbulence has been carried out. In particular, it was clearly demonstrated that the turbulence significantly influences the explosion severity by speeding up the rate of heat release on the one hand and the oxygen diffusion through the boundary layer surrounding particles on the other hand. Moreover, it modifies the mean particle size and the spatial dust distribution in the test vessel, impacting the uniformity of the dust cloud. Thus, the present work demonstrates that the procedures developed for standard tests are not sufficient to assess the dust explosivity in industrial conditions and that an extensive parametric study is relevant to figure out the explosive behavior of solid/solid mixtures subjected to variations of operating conditions.

1. Introduction

Can the explosivity of a solid/solid mixture be characterized by applying the same standardized procedures defined for a pure combustible dust? This question arises following numerous studies demonstrating that peculiar explosion behaviors can be obtained for such mixtures and showing especially that their ignition or explosion parameters cannot be deduced simply from a linear relationship based on the pure powders properties. If no 'universal equation' can be proposed, it appears that the addition of small amount of highly flammable powders has often a strong influence on the safety parameters of a less flammable dust and that the use of an 'harmonic model' based upon the powders volume fractions can be useful (Dufaud et al., 2012; Hosseinzadeh et al., 2015). In addition to the works performed on the mixtures of two flammable dusts, the opportunity of adding an inert solid to a flammable powder in order to 'moderate' the explosion risk has been explored by several authors (Addai et al., 2016; Amyotte, 2006; Danzi et al., 2015; Janes et al., 2014). Owing to the physicochemical properties of the powders, their concentration, their mechanisms (physical or

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chemical action), but also as a function of the operating conditions, the efficiency of such prevention measure is greatly variable. Such variability is also encountered with pure compounds, but if several factors may affect the explosion behavior of a dust, they can also have a different impact when considering a powders mixture. Many studies have already been carried out to identify the most important parameters: among them, turbulence is generally recognized to have a primary role (Zhang and Zhang, 2015). It affects the dust explosion severity during the pre-ignition as well as the flame propagation phases (Amyotte et al., 1989). The "cold turbulence" is issued from an intense air blast used to disperse the dust against gravity and to maintain the dust-air mixture in a "uniformly" dispersed state in the experimental apparatus. It has the feature of decaying in intensity with time (Zhen and Leuckel, 1997; Dahoe et al., 2001). Such kind of turbulence is obviously encountered not only during the experimentation phase, but also in industrial plants, resulting from the action of mechanical machinery or transportation operations, for instance. In the case of a mixture of dusts of various sizes or densities, the turbulence can also lead to segregation phenomena and the appearance of zones within the combustible cloud with slightly different composition and thus reactivity. When the turbulence intensity decreases, differential sedimentation can occur as the actual dust concentration becomes smaller, which complicates the interpretation of the experimental results (Zhen and Leuckel, 1997).

Beyond this important parameter, others factors have a great impact on the dust explosivity as well: the type and the strength of the ignition source, for instance, significantly affect the initiation and the progress of the explosion, particularly the subsequent flame propagation. Such effect is more important in the early stages of explosions and may be coupled with the influence of turbulence and with changes in the dust concentration. In the case of powders having different minimum ignition energies (MIE), the ignition energy can also be sufficient to ignite one powder but not the other one. Moreover, it should be underlined that, when the igniters' strength is overly high with regard to the MIE, a non-negligible proportion of the dust is burnt by the action of the ignitors without participating to the flame propagation. As a consequence, results may be overestimated, leading to the so called overdriven conditions (Yuan et al., 2014a). Furthermore, the combustion of the pyrotechnic igniters increases artificially the initial temperature of the system. The effect should be as reduced as possible and has to be taken into account to ensure the accuracy and repeatability of the explosion parameters measurements.

Finally the humidity can play a significant role on the dust explosivity due to heat sink, particle agglomeration or reaction kinetic inhibition (Yuan et al., 2014b). When two compounds which react differently with water are mixed, the dust mixture can exhibit peculiar (e.g. nonlinear) explosive behaviors with respect to water content. It will be notably the case when organic and metallic powders are associated: the water generated by the combustion of the organic compound or adsorbed on the particles can react with the metal at high temperature to produce hydrogen (Traoré et al., 2009).

Therefore, a deeper understanding of the manner in which those parameters influence the severity of dust mixtures is compulsory. This work aims at contributing to this issue by focalizing on solid/solid mixtures composed by graphite and metals (magnesium or iron), which can be encountered in UNGG (Uranium Natural Graphite Gas) nuclear reactors decommissioning sites.

2. Materials and methods

As said in the introduction, three powders have been specifically chosen due to their application to nuclear industry: graphite (same grade as used in graphite sleeves of UNGG reactors), magnesium and iron. These powders have also been selected with regard to their different physicochemical properties, which makes them interesting to study from a solid/solid mixtures point of view. Indeed, as shown by the Scanning Electron Microscope pictures in Fig. 1a, graphite particles are characterized by an irregular surface and it is possible to observe the presence of large particles that can be broken during the dispersion process. On the contrary, magnesium particles are perfectly spherical and smooth (Fig. 1b). The iron dust is also made of spherical particles of small sizes, but they are sometimes agglomerated in larger structures as shown in Fig. 1c. Moreover, it should be underline that the oxidation mechanisms of such powders will be strongly different due to their carbonaceous or metallic natures, but also because of the properties of their oxide layer for the metals. Thus, the Pilling and Bedworth ratio (RPB) of iron is 2.1, showing that its oxide layer is protective, which is not the case for magnesium with a RPB ratio of 0.8.

The parametric study has been carried out to observe the effect of the most relevant parameters on the severity of a 30 wt% magnesium/graphite hybrid mixture, this percentage having been chosen because of industrial applications. On the one hand, the ignition delay, the ignition energy, the relative humidity and the particle size distribution of the dust cloud have been varied in the 20 L explosion sphere (ISO 6184/1). On the other hand, the Particle Image Velocimetry technique (PIV) has been implemented in a sphere similar to the previous one both in dimensions and dust dispersion system (Fig. 2). It cannot overcome high pressures because of the presence of several portholes, but it has allowed the use of a RayPower 2000 continuous laser sheet (Dantec Dynamics) to record the dust dispersion at the geometric center of the sphere thanks to a PhantomV711 high speed video-camera with a frequency of 22,006 fps and a 640 $\times$ 480 pixels resolution. These experiments have been coupled to in situ laser granulometry analysis realized by using a laser diffraction sensor Helos-Vario/KR (SympatecGmbH), focusing on the axial plane crossing the geometrical center of the vessel (Fig. 2). The initial characteristics of the particle size distributions, especially the Sauter mean diameter $d_{3,2}$, are listed in Table 1.

Such experimental apparatus has allowed to characterize the time evolution of the turbulence intensity, to record the time evolution of the particles size distribution after the dispersion and to investigate the influence of a second solid on the dispersion phenomenon.

Finally, for some experiments carried out in the 20 L sphere, combustion gases were sampled and analyzed thanks to a four-way micro gas chromatography (GC) (Varian, CP 4900).

3. Results and discussion

At first, the severity of simple graphite dust and graphite/metal mixtures has been assessed in the 20 L explosion sphere. Then, the influence of the experimental conditions has been studied by varying several parameters (initial turbulence, particle size, ignition energy, humidity) from their standard values. The experimental reproducibility has been investigated by performing the same explosion test four times at stoichiometry and then by assuming the same standard deviation for other fuel concentrations. It appears that a deviation of 3.5% could be assessed for the maximum explosion pressure and of 11% for the maximum rate of pressure rise, which is in good agreement with the values presented by Proust et al. (2007).

3.1. Influence of initial turbulence level

A dust cloud can be ignited with a defined delay from the